

**UNCLASSIFIED**

**AD 408 443**

**DEFENSE DOCUMENTATION CENTER**

**FOR**

**SCIENTIFIC AND TECHNICAL INFORMATION**

**CAMERON STATION, ALEXANDRIA, VIRGINIA**



**UNCLASSIFIED**

NOTICE: When government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related government procurement operation, the U. S. Government thereby incurs no responsibility, nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.

634

CATALOGED BY DDC  
408443  
AS AD NO.

ONR TECHNICAL REPORT  
NO. 51

Project: NR 356-378

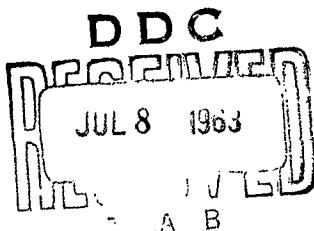
Contract: Nonr 3357(01)

Principal Investigator: Richard S. Stein

408443

THE DETERMINATION OF BIAXIAL ORIENTATION  
BY X-RAY DIFFRACTOMETRY

September 10, 1962



C. RICHARD DESPER  
POLYMER RESEARCH INSTITUTE  
University of Massachusetts, Amherst, Mass.

ABSTRACT

The state of biaxial orientation of crystallites of a polycrystalline polymer may be determined by measuring the x-ray diffracted intensity from particular crystal planes (at a fixed Bragg angle) as a function of the azimuthal diffracted angle and of the sample tilt angle. The orientation distribution may be expressed in terms of two dimensional pole-figure projections or in terms of biaxial orientation functions.

Geometric relations governing the determination of such pole-figures are stated, and a computer program is presented for their calculation. Correction factors for absorption, polarization and incoherent scattering are included in the program.

# The Determination of Biaxial Orientation by X-Ray Diffractometry\*

C. Richard Desper<sup>+</sup>  
Polymer Research Institute  
University of Massachusetts, Amherst, Massachusetts

## INTRODUCTION

Previous authors<sup>1,2</sup> have studied uniaxial orientation in polymer films from x-ray diffracted intensity data. Intensity data have been obtained using an automatized diffractometer described previously<sup>3</sup> and the IBM 1620 Computer at the University of Massachusetts has been programmed<sup>2</sup> to correct for background, polarization, absorption, and incoherent scatter.

To determine the more general biaxial orientation functions described by Stein<sup>4</sup>, modifications of the x-ray diffractometer and of the intensity correction procedures are required. A new computer program has been obtained to perform these corrections.

## GEOMETRIC RELATIONS

A. Specification of Orientation: The methods for completely specifying the orientation of crystals having an orthorhombic unit cell, such as polyethylene, have been described by Stein<sup>4</sup>. In the present work it will be assumed that the experimenter is studying the orientation of only one crystal plane, say the 200 plane of polyethylene.<sup>†</sup> The orientation of such

---

\* Supported in part by contracts with the Office of Naval Research and the Atomic Energy Commission and grants from the Flax Corporation and the Petroleum Research Fund.

+ Flax Graduate Fellow

† Chosen only as an illustration. The discussion could apply equally well to any diffracting plane of any crystalline polymer.

a plane is described by two angles,  $\alpha$  and  $\delta$ , at which the plane normal (in this case, the a axis) is oriented with respect to the film coordinates (Fig.1). In the general case, the number of plane normals oriented in a given direction will be a function of both  $\alpha$  and  $\delta$ .

One possible visualization of the orientation distribution is to imagine the polymer sample to be surrounded by a transparent sphere, with any point on the surface being specified by the angles  $\alpha$  and  $\delta$ , as before (see Fig. 2).

In analogy to geography, the  $z'$  axis (stretch direction) may be thought of as the "north pole" and the angle  $\delta$  as "longitude", measured from the  $y' z'$  plane (plane of the film). Associated with every point  $(\alpha, \delta)$ , on the surface of the sphere is a quantity  $N(\alpha, \delta)$  which is proportional to the density of a axes at that point.

B. Preparation of Pole Figures: A more convenient graphical illustration of the distribution of a crystal direction, such as the a axis, is afforded by the two-dimensional pole figure plot, described by various authors<sup>5,6</sup>. The imaginary sphere is cut by a plane passing through its center, and all points on the surface of the sphere are mapped into this plane by a polar projection. Points in one hemisphere are projected into the plane of the pole figure on a line passing through the opposite pole, and vice versa. Thus, all points on the surface of the sphere will map inside a great circle, called the basic circle, described by the intersection of the sphere and the plane of the pole figure. Points from the two hemispheres may be distinguished by using x's for one and o's for the other.

It is apparent that any number of pole figures may be prepared, depending upon the choice of the intersecting plane. In this work, two pole figures will be considered:

- a) Pole figure centered about stretch direction.
- b) Pole figure centered about film normal.

Referring to Figure 1, the first pole figure is constructed by a cut through the  $x'y'$  plane (normal to stretch direction) and the second by a cut through the  $z'y'$  plane (plane of the film). Both pole figures will contain the same information, but presented in a different manner. The data output of the computer program given here will allow the experimenter to prepare either pole figure at his discretion.

The location of a point within a pole figure is defined by two quantities, a radius and an angle (Fig. 3). For the pole figure centered about the stretch direction the angle can be taken as the angle  $\delta$ , which is preserved without distortion during the polar projection. Assuming the basic circle to be of unit radius it can be shown (Appendix V) that  $r$  is given by

$$r = \sqrt{\frac{1 - |\cos \alpha|}{1 + |\cos \alpha|}} \quad (1)$$

The absolute value signs compensate for the fact that the projection is taken from two different poles, depending upon the magnitude of  $\alpha$ . An explicit expression is given later in this work for  $\cos \alpha$ , allowing one to distinguish between the two hemispheres by noting the sign of  $\cos \alpha$ . For the pole figure centered about the film normal, it is necessary to define two new angles,  $\alpha'$  and  $\delta'$  (Fig. 4). The angle  $\alpha'$  is the angle between the a axis and the  $x'$  (film normal) axis;  $\delta'$  is the angle in the  $y'z'$  (film) plane between the  $y'$  direction and the projection of the a axis. The loca-

tion of a point on the pole figure (see Figure 5) is defined by the angle  $\delta'$  and a radius  $r'$  given by

$$r' = \sqrt{\frac{1 - |\cos \alpha'|}{1 + |\cos \alpha'|}} \quad (2)$$

C. Spectrometer Geometry: Measurements of x-ray diffraction intensity will be made on the automatic x-ray diffractometer described in a previous report<sup>3</sup> modified to include provisions for tilting the sample. The sample will be considered to be mounted at the beginning of the scan with the stretching direction vertical and the plane of the film bisecting the angle between the incident and diffracted beams, as shown in Figure 6. The diffractometer coordinates are taken so that the z-axis is vertical (perpendicular to the plane of the diffractometer) and the x-axis makes an angle  $\theta_{200}$  with both the incident and diffracted beams. The angle  $\theta_{200}$  is chosen to satisfy the Bragg condition:

$$\lambda = 2 d_{200} \sin \theta_{200} \quad (3)$$

The choice of coordinates differs from those of a previous report<sup>9</sup> in which the x-axis was taken along the incident beam.

When the sample is first mounted, the x y z (diffractometer) coordinate axes will coincide with the x' y' z' (film) axes. The film is then rotated through an azimuthal angle  $\psi$  and a tilt angle  $\phi$  as shown in Figure 7.

The condition for constructive interference of diffracted x-rays is:

$$\frac{\underline{H}}{\sim} = \frac{\underline{S} - \underline{S}_0}{\lambda} \quad (4)$$

where  $\underline{S}$  is a unit vector in the diffracted beam,  $\underline{S}_0$  is a unit vector along

the incident beam,  $\underline{H}$  is the reciprocal lattice vector perpendicular to the crystal plane being detected, and  $\lambda$  is the wave length of the x-rays. From this equation it is apparent that the  $\underline{H}$  vector will always lie along the y-axis.

Stein<sup>8</sup> gives the following relations for  $\cos \alpha$  and  $\cos \delta$ , based on an azimuthal angle  $\Omega$  and a tilt angle  $\phi'$ , defined upon a different set of diffractometer coordinates:

$$\cos \alpha = \cos \Omega \cos(\theta - \phi') \quad (5)$$

$$\cos \delta = \frac{\cos \alpha \sin \Omega}{\sin \alpha \cos \Omega} \quad (6)$$

The relations to the angles of this report are:

$$\phi = \theta - \phi' \quad (7)$$

$$\psi = \frac{\pi}{2} - \Omega \quad (8)$$

Substituting and using the relation

$$\sin \alpha = +\sqrt{1 - \cos^2 \alpha} \quad (9)$$

yields the following:

$$\cos \alpha = \sin \psi \cos \phi \quad (10)$$

$$\cos \delta = \frac{\cos \phi \cos \psi}{\sqrt{1 - \sin^2 \psi \cos^2 \phi}} \quad (11)$$

It can be easily shown that  $\sin \delta$  is given by:

$$\sin \delta = \frac{-\sin \phi}{\sqrt{1 - \sin^2 \psi \cos^2 \phi}} \quad (12)$$

These geometric quantities, along with the corresponding corrected intensities, may be used either to compute orientation functions or to plot a pole figure centered about the stretch direction.

Comparing Figures 4 and 7, it is apparent that the angles  $\alpha'$  and  $\delta'$  are given by:

$$\alpha' = \frac{\pi}{2} + \phi \quad (13)$$

$$\delta' = \psi \quad (14)$$

Thus the pole figure centered about the film normal is easily constructed from data on  $\psi$ ,  $\phi$ , and the corresponding corrected x-ray intensity.

#### X-RAY INTENSITY CORRECTION

A. Correction for Non-Tilted Samples: The experimental x-ray intensity must be corrected for background, polarization, absorption, and incoherent scattering before being used to obtain orientation functions. A previous report<sup>2</sup> gives the following relation for correcting x-ray intensity:

$$I = (I_{\text{exp}} - I_{\text{backg}}) \cdot C_{\text{pol}} \cdot C_{\text{abs}} - I_{\text{incoh}} \quad (15)$$

where

$I$  = corrected intensity

$I_{\text{exp}}$  = experimental intensity

$I_{\text{backg}}$  = background intensity, determined at the same Bragg angle with the sample removed

$C_{\text{pol}}$  = polarization correction factor

$C_{\text{abs}}$  = absorption correction factor, and

$I_{\text{incoh}}$  = incoherent scattering intensity.

The polarization correction factor is given by

$$C_{\text{pol}} = \frac{1 + \cos^2 2 \theta_M}{1 + \cos^2 2 \theta_M \cos^2 2 \theta} \quad (16)$$

where

$\theta_M$  = Bragg angle for the monochromatizing crystal.

The quantity  $C_{\text{abs}}$  is dependent upon the tilt angle  $\phi$ . The previous report<sup>2</sup> gives the following relation for a non-tilted sample ( $\phi = 0^\circ$ ):

$$C_{\text{abs}} = \cos \theta e^{-\mu d \sec \theta} \quad (17)$$

where  $\mu$  = linear absorption coefficient

$d$  = sample thickness

Incoherent scattering is given by the following equation<sup>2</sup>:

$$I_{\text{incoh}} = C_{\text{incoh}} \left[ \sum_i \left\{ z_i - \sum_j f_j^2 \right\} \right] \quad (18)$$

where

$C_{\text{incoh}}$  = experimentally determined coefficient

$z_i$  = atomic number of the  $i^{\text{th}}$  atom of the sample.

$\sum_j f_j^2$  = atomic form factor for the  $i^{\text{th}}$  atom for scattering at  $2\theta$ .

$C_{\text{incoh}}$  is evaluated by assuming that the scattering is completely incoherent; i.e.  $I = 0$ , at a sufficiently high Bragg angle, arbitrarily set at  $2\theta = 50^\circ$ .

It is apparent that the scattering volume of the sample will increase as the x-ray beam is tilted away from normal incident to  $\theta$  incidence. The factor  $\cos \theta$  in the expression for  $C_{\text{abs}}$  compensates for this effect to reduce the intensity to a basis of constant scattering volume.

B. Correction for Tilted Sample: When the sample is tilted away from the  $\phi = 0^\circ$  position the scattering volume and the path length through the sample are altered, resulting in changes in  $C_{abs}$ . Two integrated expressions for  $C_{abs}$  have been obtained (see Appendix VI), one appropriate for the transmission method and one appropriate for the reflection method.

These expressions are:

Transmission -

$$C_{abs} = |\cos(\theta-\phi)| \frac{\mu d(|\sec(\theta+\phi)| - |\sec(\theta-\phi)|)}{\exp(-\mu d|\sec(\theta-\phi)|) - \exp(-\mu d|\sec(\theta+\phi)|)} \quad (19)$$

Reflection -

$$C_{abs} = |\cos(\theta-\phi)| \frac{\mu d(|\sec(\theta+\phi)| + |\sec(\theta-\phi)|)}{1 - \exp[-\mu d|\sec(\theta+\phi)|] - \mu d|\sec(\theta-\phi)|} \quad (20)$$

It can be shown (Appendix VII) that transmission occurs when the quantities  $\cos(\theta+\phi)$  and  $\cos(\theta-\phi)$  have the same sign, while reflection occurs when the signs are opposite. Thus, for transmission, the product of the two quantities is positive; for reflection, negative. The product cannot be zero since in such a case either the incident beam or the diffracted beam would be blocked by the sample holder.

#### COMPUTER PROGRAM

The program was written using the FORTRAN compiling system of programming for the IBM 1620 computer. A listing of the program is given in Appendix I; a flow chart is shown in Appendix II; Appendix III contains a glossary of symbols used in the program; and Appendix IV contains a set of operating notes.

To execute the program, the quantities COS2, AB, THK, CCO, BRAG, BT, and STRF are entered from the typewriter. The experimental data, consisting of the tilt angle PHID, azimuthal angle PSID, and TEXP, the time for 1000 counts, are read from a punched card. The computer chooses the appropriate expression for CABS, the absorption correction factor, and computes the corrected x-ray intensity, CINT, followed by the quantities COSD, COSA, and RAD.

The output, consisting of PHID, PSID, COSD, COSA, RAD and CINT is either printed or punched\*, according to the setting of Sense Switch 1. The machine then reads another data card and repeats the calculation from that point. It will continue in this manner until it reads a data card on which the TEXP is a negative quantity or zero. This serves as a signal that all the data from a given Bragg angle has been computed, and the machine will return to the top of the program to accept new values of COS2, ABS, THK, CCO, BRAG, BT, and STRF.

The output suffices to completely specify the orientation of the diffracting plane. The angle  $\alpha$  is identified by COSA or  $\cos\alpha$ , since  $\alpha$  is limited to the range  $0 \leq \alpha \leq \pi$ . COSD (or  $\cos\delta$ ) alone is not sufficient to specify  $\delta$ , since the cosine function is symmetric with respect to  $\delta = 0$ . This degeneracy can be removed by noting the sign of  $\sin\delta$ , which is given by:

$$\sin\delta = \frac{-\sin\psi}{\sqrt{1-\sin^2\psi \cos^2\psi}} \quad (21)$$

Hence,  $\sin\delta$  and  $\sin\psi$  are always opposite in sign, and the quantities PHID and COSD suffice to specify  $\delta$ .

With a minimum of effort, either of the two pole figures previously referred to may be prepared. Alternately, the values COSA and COSD may be used to compute orientation functions.

\*If the punch is chosen, the first card punched will contain the Bragg angle.

-10-

An example of some input and output data in the execution of this program is given in Appendix VIII.

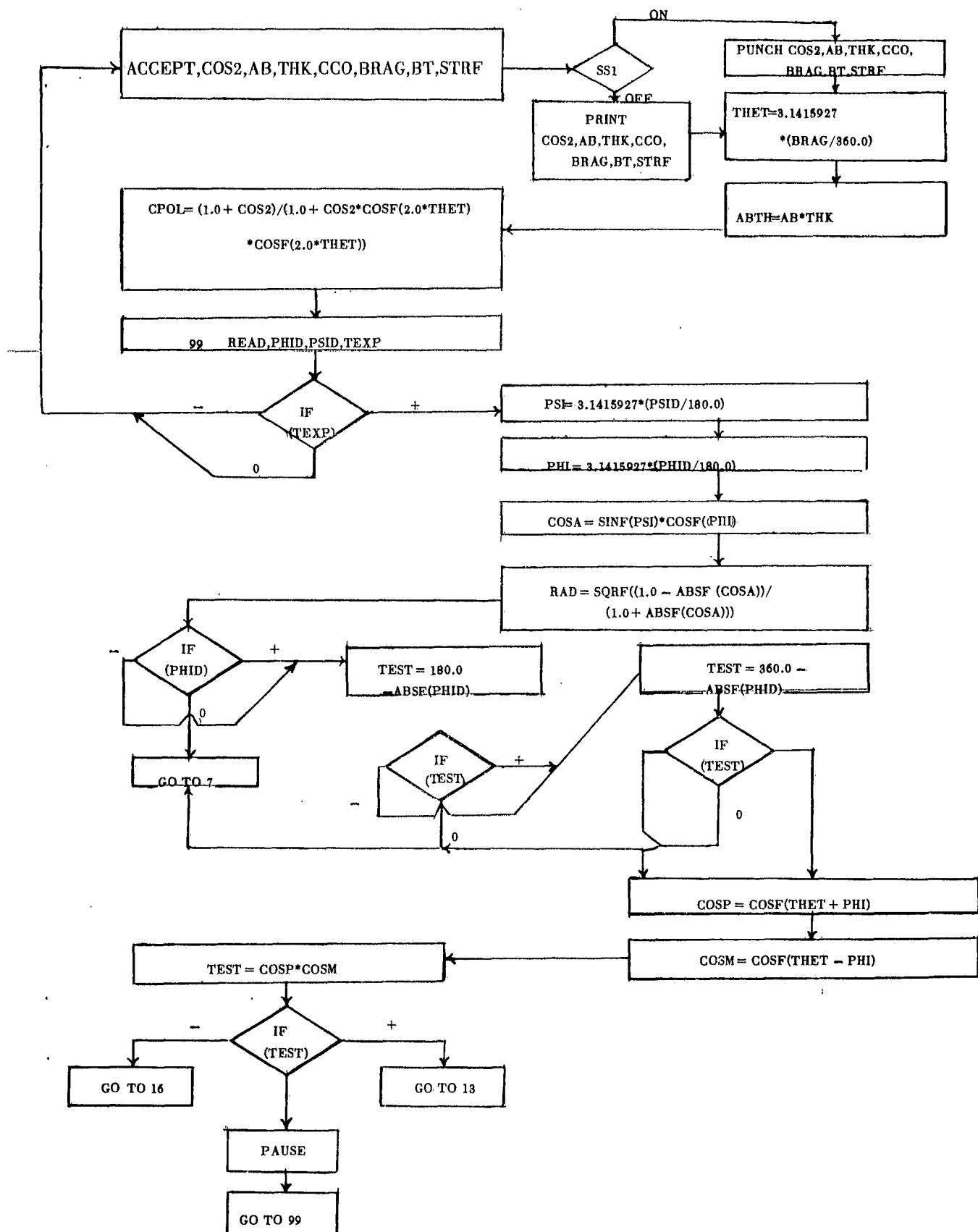
APPENDIX I  
LISTING OF PROGRAM

```
C      FORTRAN PROGRAM - BIAXIAL XRAY SCAN
100    ACCEPT 40,COS2,AB,THK,CCO
          ACCEPT 40,BRAG,BT,STRF
          IF (SENSE SWITCH 1) 1,20
1        PUNCH 45,COS2,AB,THK,CCO,BRAG,BT,STRF
          GO TO 3
20       PRINT 45,COS2,AB,THK,CCO,BRAG,BT,STRF
3        THET=3.1415927*(BRAG/360.0)
          ABTH=AB*THK
          CPOL=(1.0+COS2)/(1.0+COS2*COSF(2.0*THET)*COSF(2.0*THET))
99       READ 40,PHID,PSID,TEXP
          TEST FOR END CARD
          IF (TEXP) 100,100,5
5        PSI=3.1415927*(PSID/180.0)
          PHI=3.1415927*(PHID/180.0)
19       COSA=SINF(PSI)*COSF(PHI)
          RAD=SQR((1.0-ABSF(COSA))/(1.0+ABSF(COSA)))
C      TEST FOR TILT
          IF (PHID) 6,7,6
6        TEST=180.0-ABSF(PHID)
          IF (TEST) 11,7,11
11      TEST=360.0-ABSF(PHID)
          IF (TEST) 15,7,15
C      TESTS FOR REFLECTION OR TRANSMISSION
15       COSP=COSF(THET+PHI)
          COSM=COSF(THET-PHI)
          TEST=COSP*COSM
          IF (TEST) 16,12,13
12      PAUSE
          GO TO 99
C      UNTILTED SAMPLE
7        CABS=COSF(THET)*EXP(ABTH/COSF(THET))
          TEST=COSF(PSI)*COSF(PHI)
          IF (TEST) 17,4,18
17      COSD=-1.0
          GO TO 8
4        COSD=0.0
          GO TO 8
18      COSD=1.0
          GO TO 8
```

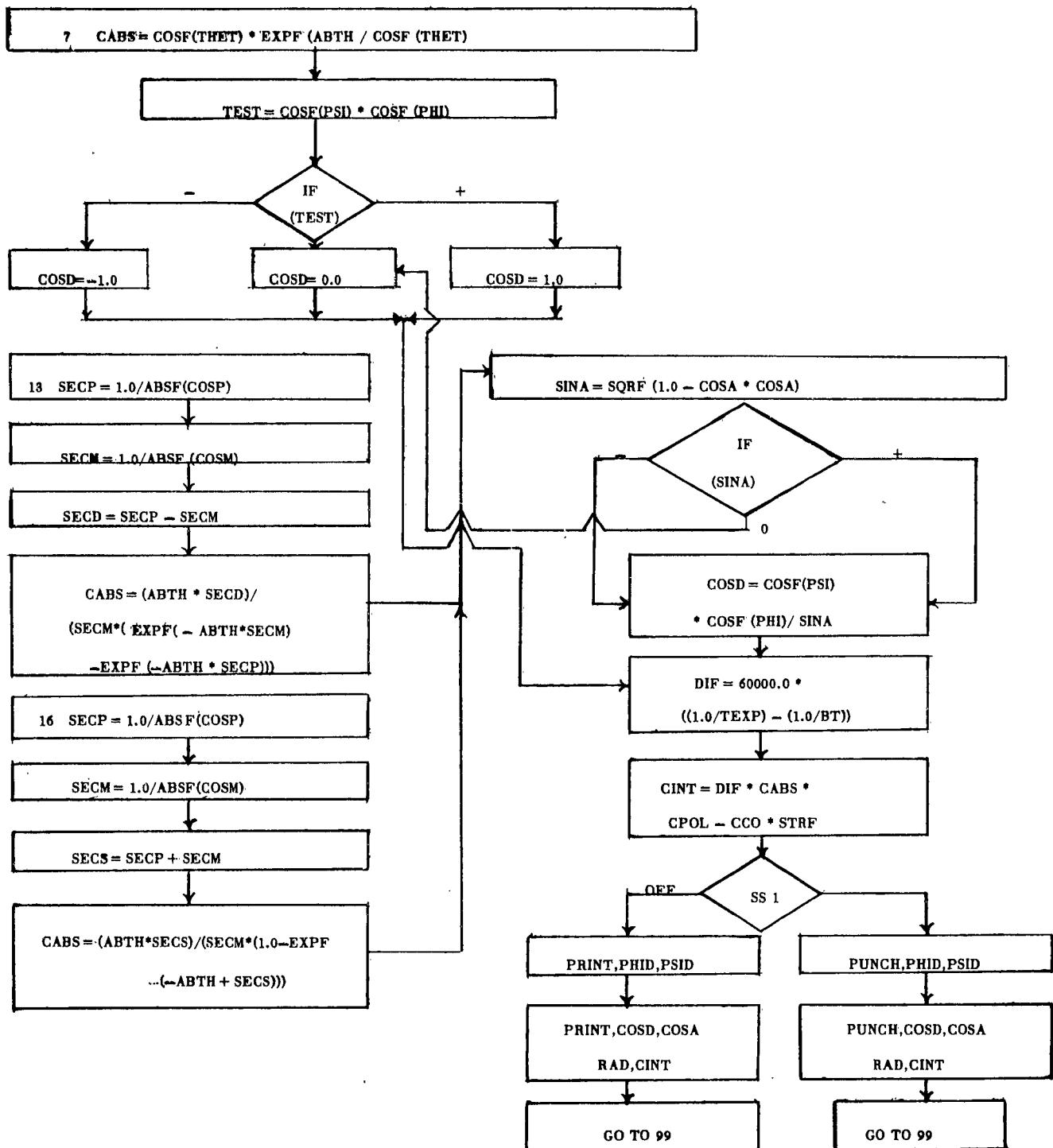
App.I --Cont.

C           TRANSMISSION METHOD  
13        SECP=1.0/ABSF(COSP)  
          SECM=1.0/ABSF(COSM)  
          SECD=SECP-SECM  
          CABS=(ABTH\*SECD)/(SECM\*(EXP(-ABTH\*SECM)-EXP(-ABTH\*SECP)))  
          GO TO 14  
C           REFLECTION METHOD  
16        SECP=1.0/ABSF(COSP)  
          SECM=1.0/ABSF(COSM)  
          SECS=SECP+SECM  
          CABS=(ABTH\*SECS)/SECM\*(1.0-EXP(-ABTH\*SECS)))  
14        SINA=SQRF(1.0-COSA\*COSA)  
          IF (SINA) 2,4,2  
2           COSD=COSF(PSI)\*COSF(PHI)/SINA  
8           DIF=60000.0\*((1.0/TEXP)-(1.0/BT))  
          CINT=DIF\*CABS\*CPOL-CCO\*STRF  
          IF (SENSE SWI TCH 1) 9,10  
9           PUNCH 50,PHID,PSID,COSD,COSA,RAD,CINT  
          GO TO 99  
10          PRINT 50,PHID,PSID,COSD,COSA,RAD,CINT  
          GO TO 99  
40          FORMAT(F10.5,F10.5,F10.5,F10.5)  
45          FORMAT(F7.4,F6.3,F8.5,F7.4,F5.1,F7.1,F6.2)  
50          FORMAT(F6.1,F6.1,F8.5,F8.5,F8.5,F8.2)  
          END

APPENDIX II - FLOW CHART OF PROGRAM



-continued-



APPENDIX III  
GLOSSARY OF SYMBOLS USED IN BIAXIAL X-RAY SCAN PROGRAM

AB	= $\mu$ , linear absorption coefficient in centimeters <sup>-1</sup> *
BRAG	= $2\theta$ , diffraction angle in degrees
BT	= background time at $2\theta$ in seconds/1000 count
CCO	= $C_{ineoh}$ from radial scan in counts/minute
CINT	= I, corrected intensity in counts/minute
COS2	= $\cos^2(2\theta_M) = 0.8830$ for 111 plane of germanium
COSA	= $\cos \alpha$
COSD	= $\cos \delta$
PHID	= $\phi$ tilt angle in degrees
PSID	= $\psi$ azimuthal angle in degrees
RAD	= $r = \sqrt{\frac{1-1\cos\alpha}{1+1\cos\alpha}}$
STRF	= $\sum_i \{ z_i - \sum_j f_j^2 \}$ evaluated at $2\theta$
TEXP	= time for 1000 counts with sample in position
THK	= sample thickness, centimeters*

\* Any set of consistent units can be used for AB and THK, e.g., inches and inches<sup>-1</sup>

APPENDIX IV  
OPERATING NOTES FOR BIAXIAL X-RAY SCAN

1. Clear Memory
2. Insert Object Program
3. Sense Switch 1 ON for punched output, OFF for printed output. If punch option is chosen, load blank cards into the punch hopper and push PUNCH START.
4. Type COS2, AB, THK, CCO - RELEASE START (See Note 1 )
5. Place data cards in read hopper, push READER START (See Note 2).
6. Information punched out will be: COS2 AB THK CCO BRAG BT STRF PHID PSID  
COSD COSA RAD CINT
7. To process data for a second sample or a second Bragg angle, place an "end card" at the end of the first data card deck (See Note 3). Then repeat (3) - (6).

## OPERATING NOTES

### NOTE 1

The quantities COS2, AB, THK, etc. should all be in floating point form. (See Appendix III for a Glossary of Symbols). Leave at least one space between data entries. Ten spaces are reserved for each entry, so COS2 should be types within the first ten spaces, AB in the second ten spaces, etc.

### NOTE 2.

Format for data cards.

<u>PHID</u>	<u>PSID</u>	<u>TEXP</u>
-30.0	0.0	87.4
-15.0	0.0	89.1
0.0	0.0	72.0
+15.0	5.0	110.4      etc.

Data cards need not be in any particular order. Ten spaces are reserved for each entry, so PHID should be in columns 1-10, PSID in columns 11-20, and TEXP in columns 21-30.

### NOTE 3

Example of an "end card"

0.0            0.0            -1.0

The quantities PHID and PSID are arbitrary; any floating point numbers will do. The quantity TEXP should be negative or zero, and in floating point form.

### NOTE 4

The program will pause if it reads a tilt angle such that  $\cos(\theta + \phi) = 0$ , or  $\cos(\theta - \phi) = 0$ . Such a tilt angle is unrealistic since the sample holder would be blocking either the incident or the diffracted beam. In such a case, push START and the machine will ignore the data and proceed to the next card.

### NOTE 5

The expression for COSD becomes indeterminate (0/0) when  $\sin \alpha = 0$ . In such a case, the angle  $\delta$  cannot be defined; however, the computer is programmed to assign the arbitrary value COSD = 0.0 in such a case.

## APPENDIX V

### THE POLE FIGURE PROJECTION

Refer to Figure 8. A point A, assumed (for the moment) to be in the northern hemisphere, is projected into the equatorial plane by a line passing through S, the south pole.

The radial location  $r$  in the equatorial plane is given by

$$r = \tan \rho \quad (21)$$

Since the angle  $\rho$  subtends a central angle  $\alpha$ , the following holds:

$$\rho = \frac{\alpha}{2} \quad (22)$$

Hence,

$$r = \tan \frac{\alpha}{2} \quad (23)$$

but  $\tan \frac{\alpha}{2}$  is given by:

$$\tan \frac{\alpha}{2} = \sqrt{\frac{1 - \cos \alpha}{1 + \cos \alpha}} \quad (24)$$

By substitution,

$$r = \sqrt{\frac{1 - \cos \alpha}{1 + \cos \alpha}} \quad (25)$$

Now assume point A is in the southern hemisphere. The same equation holds if  $\alpha$  is replaced by  $(\pi - \alpha)$ . Hence,

$$r = \sqrt{\frac{1 - \cos(\pi - \alpha)}{1 + \cos(\pi - \alpha)}} = \sqrt{\frac{1 + \cos \alpha}{1 - \cos \alpha}} \quad (26)$$

App. V cont.

Since  $\cos \alpha$  is positive in the northern hemisphere and negative in the southern hemisphere, the following holds in both hemispheres:

$$r = \sqrt{\frac{1 - |\cos \alpha|}{1 + |\cos \alpha|}} \quad (27)$$

## APPENDIX VI

### ABSORPTION FORMULAS

#### A. Transmission Method

Figure 9 shows the sample tilted at an angle  $\phi$ . The incident beam makes an angle  $(\theta - \phi)$  with the film normal; the diffracted beam makes an angle  $(\theta + \phi)$  with the normal.

If no reflection occurs, the path length  $\ell$  is given by

$$\ell = \overline{AB} = D |\sec (\theta - \phi)| \quad (28)$$

If reflection occurs at the leading edge of the sample (point B), the path length  $\ell$  is

$$\ell = \overline{BC} = d |\sec (\theta - \phi)| \quad (29)$$

In general, if the beam is reflected after traversing a fraction  $f$  of the sample,  $\ell$  is given by:

$$\ell (f) = d \left[ f |\sec (\theta - \phi)| + (\ell - f) |\sec (\theta + \phi)| \right] \quad (30)$$

The attenuation  $A$  of such a beam due to sample absorption is

$$A(f) = e^{-\mu \ell (f)} \quad (31)$$

The average attenuation  $\langle A \rangle$  due to sample absorption is given by

$$\langle A \rangle = \frac{\int_0^1 A(f) df}{\int_0^1 df} \quad (32)$$

App. VI cont.

Substituting and integrating,

$$\langle A \rangle = \frac{\exp[-\mu d |\sec(\theta - \phi)|] - \exp[-\mu d |\sec(\theta + \phi)|]}{\mu d |\sec(\theta - \phi)| - \mu d |\sec(\theta + \phi)|} \quad (33)$$

However, the scattering volume of the sample increases when the incident beam is tilted away from the film normal. This increase is given by:

$$V/V_0 = |\sec(\theta - \phi)| \quad (34)$$

The proper expression for  $C_{abs}$  is:

$$C_{abs} = \frac{V_0}{\langle A \rangle V} \quad (35)$$

Substituting (33) and (34) into (35):

$$C_{abs} = |\cos(\theta - \phi)| \frac{\mu d |\sec(\theta + \phi)| - \mu d |\sec(\theta - \phi)|}{\exp[-\mu d |\sec(\theta - \phi)|] - \exp[-\mu d |\sec(\theta + \phi)|]} \quad (36)$$

Note that this expression becomes indeterminate (0/0) when  $\theta = 0, \pm \pi, \pm 2\pi$ , etc. where the untilted formula applies.

#### B. Reflection Method

Figure 10 shows a sample in position to observe diffraction via the reflection method. If reflection occurs at the leading edge of the sample (point A), there is no absorption and  $\ell$  is given by:

$$\ell = 0 \quad (37)$$

If reflection occurs at the trailing edge of the sample,  $\ell$  is given by:

$$\ell = \overline{AB} + \overline{BD} \quad (38)$$

App. VI cont..

Hence, it is necessary to solve the triangle ABD. By inspection,

$$\angle BAD = \angle CBA = \theta - \phi + \frac{\pi}{2} \quad (39)$$

$$\angle BDA = \angle EBA = \theta + \phi - \frac{\pi}{2} \quad (40)$$

Length  $\overline{AB}$  is given by

$$\overline{AB} = d |\csc \angle CBA| = d |\sec (\theta - \phi)| \quad (41)$$

For length  $\overline{BD}$ , use the law of sines on triangle ABD:

$$\frac{\sin \angle BAD}{\overline{BD}} = \frac{\sin \angle BDA}{\overline{AB}} \quad (42)$$

Substituting (39), (40) and (41) into (42):

$$\overline{BD} = \overline{AB} \left| \frac{\cos (\theta - \phi)}{\cos (\theta + \phi)} \right| \quad (43)$$

By substitution, the length  $\underline{l}$  is given by:

$$\underline{l} = d |\sec (\theta - \phi)| + d |\sec (\theta + \phi)| \quad (44)$$

If reflection takes place at F after traversing a fraction f of the sample, the path length is:

$$l(f) = \overline{AF} + \overline{FG} \quad (45)$$

Since triangles AFG and ABD are similar the following holds:

$$l(f) = f(\overline{AB} + \overline{BD}) = fd \left[ |\sec (\theta - \phi)| + |\sec (\theta + \phi)| \right] \quad (46)$$

## APPENDIX VII

### CONDITIONS FOR REFLECTION OR TRANSMISSION

Figure 11 shows the areas in which reflection occurs and the areas in which transmission occurs. By inspection the angle  $\phi$  must satisfy two conditions for reflection to occur:

$$\phi > \frac{\pi}{2} - \theta + n\pi$$

and

$$\phi < \frac{\pi}{2} + \theta + n\pi$$

where  $n$  is 0,  $\pm 1$ ,  $\pm 2$ , etc. Re-arranging the inequalities:

$$\phi + \theta > \frac{\pi}{2} + n\pi$$

$$\phi - \theta < \frac{\pi}{2} + n\pi$$

If  $n$  is even,  $\cos(\phi + \theta)$  is negative and  $\cos(\phi - \theta)$  [or  $\cos(\theta - \phi)$ ] is positive. If  $n$  is odd, the reverse is true. In either case, the two quantities always have opposite signs for reflection.

For transmission it is necessary to negate one of the conditions for reflection. For instance,

$$\phi + \theta > \pi/2 + n\pi$$

and

$$\phi - \theta > \pi/2 + n\pi$$

Alternately,

$$\phi + \theta < \pi/2 + n\pi$$

and

$$\phi - \theta < \pi/2 + n\pi$$

In either case,  $\cos(\theta + \phi)$  and  $\cos(\theta - \phi)$  will have the same sign.

## APPENDIX VIII

### SAMPLE PROBLEM

Data typed in:

COS2	AB	THK	CCO	BRAG	BT	STRF
0.8830	4.44	0.00762	1.9234	21.1	685.6	2.26

Data fed in on cards:

PHID	PSID	TEXP
12.0	60.0	113.9
6.0	60.0	119.3
0.0	60.0	116.3
-6.0	60.0	128.9
-12.0	60.0	132.8
-36.0	0.0	180.1
0.0	0.0	141.3

Output:

COS2	AB	THK	CCO	BRAG	BT	STRF
.8830	4.440	.00762	1.9234	21.1	685.6	2.26

PHID	PSID	COSD	COSA	RAD	CINT
12.0	60.0	.92029	.84710	.28771	479.95
6.0	60.0	.97861	.86128	.27299	452.08
0.	60.0	1.00000	.86602	.26794	459.75
-6.0	60.0	.97861	.86128	.27299	394.98
-12.0	60.0	.92029	.84710	.28771	366.70
-36.0	0.	.80901	.00000	1.00000	183.47
0.	0.	1.00000	.00000	1.00000	360.86

#### REFERENCES

1. D. LeGrand, Ph.D. Thesis, "A Study of Molecular Orientation in Polyethylene", University of Massachusetts, 1959.
2. R. S. Stein, J. Powers and S. Hoshino, ONR Technical Report No.33, Project 356-378, Contract Nonr 3357(01), July 7, 1961, University of Mass., Amherst, Mass.
3. D. LeGrand, D. Keedy and R. S. Stein, ONR Technical Report No.26, Project NR356-378, Contract Nonr 3357(01), May 1, 1961, University of Mass., Amherst, Mass.
4. R. S. Stein, J. Polymer Sci., 31, 327, 335 (1958)
5. H. P. Klug and L. E. Alexander, X-Ray Diffraction Procedures, John Wiley, New York (1954) pp. 568-585
6. A. Hargreaves, "Methods of Examining Orientation Texture" in H. S. Peiser, H. P. Rookes, and A. J. C. Wilson (Editors), X-Ray Diffraction by Polycrystalline Materials, Reinhold, New York (1955) 316-320
7. B. Decker, E. T. Asp, and D. Harker, J. Appl. Phys., 19, 388 (1948)
8. R. S. Stein, ONR Technical Report No.8, Project NR 356-378, Nov. 13, 1958, University of Mass., Amherst, Mass.

CAPTIONS FOR FIGURES

- Figure 1 Orientation of polyethylene crystal with respect to film coordinates.
- Figure 2 Location of an a axis on the surface of a sphere.
- Figure 3 Pole Figure centered about stretch direction.
- Figure 4 Orientation of an a axis with respect to film normal.
- Figure 5 Pole Figure centered about film normal.
- Figure 6 Diffractometer coordinates.
- Figure 7 Motions of film coordinates with respect to diffractometer coordinates.
- Figure 8 The Pole Figure projection.
- Figure 9 Diffraction geometry - transmission method.
- Figure 10 Diffraction geometry - reflection method.
- Figure 11 Regions of reflection or transmission.

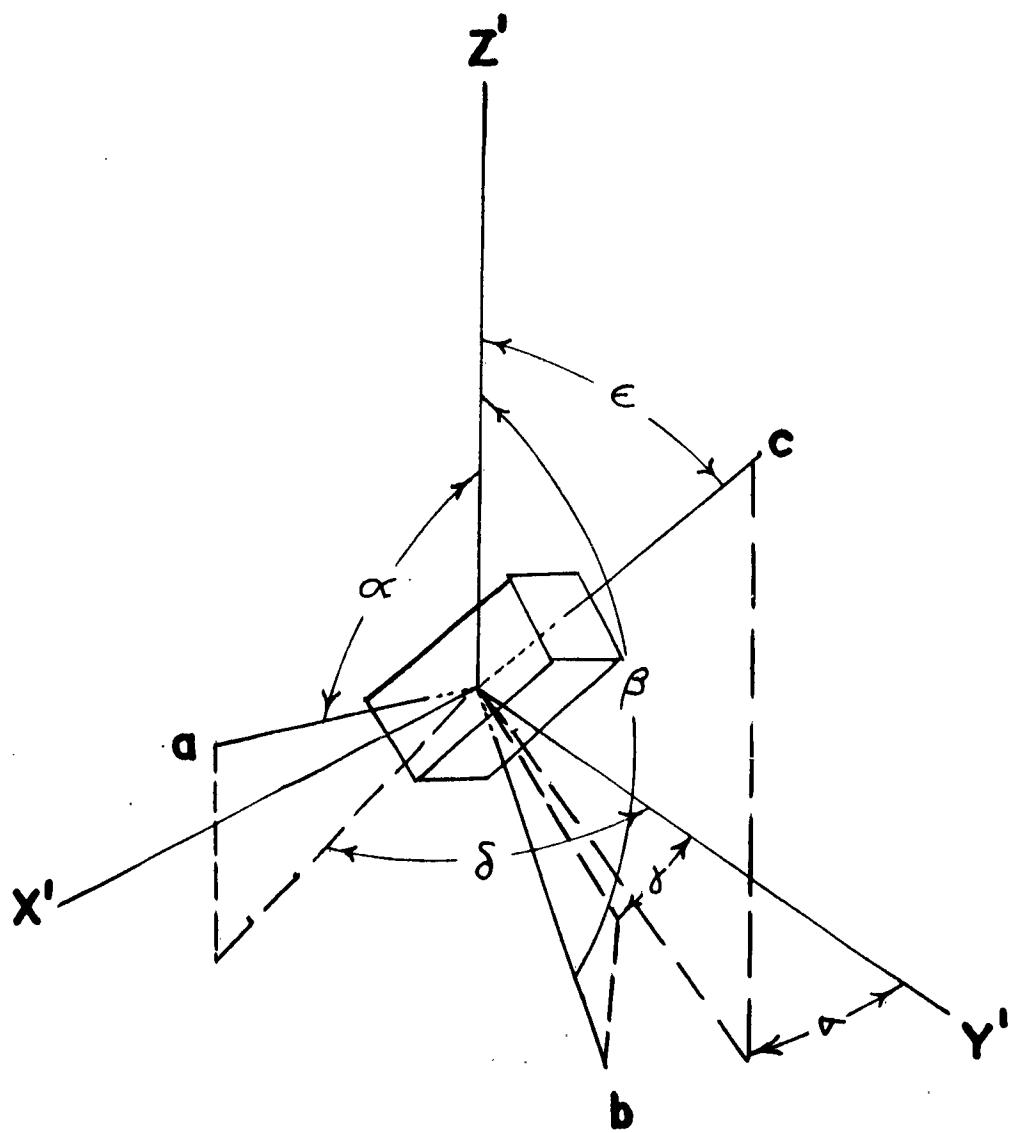


Fig. I

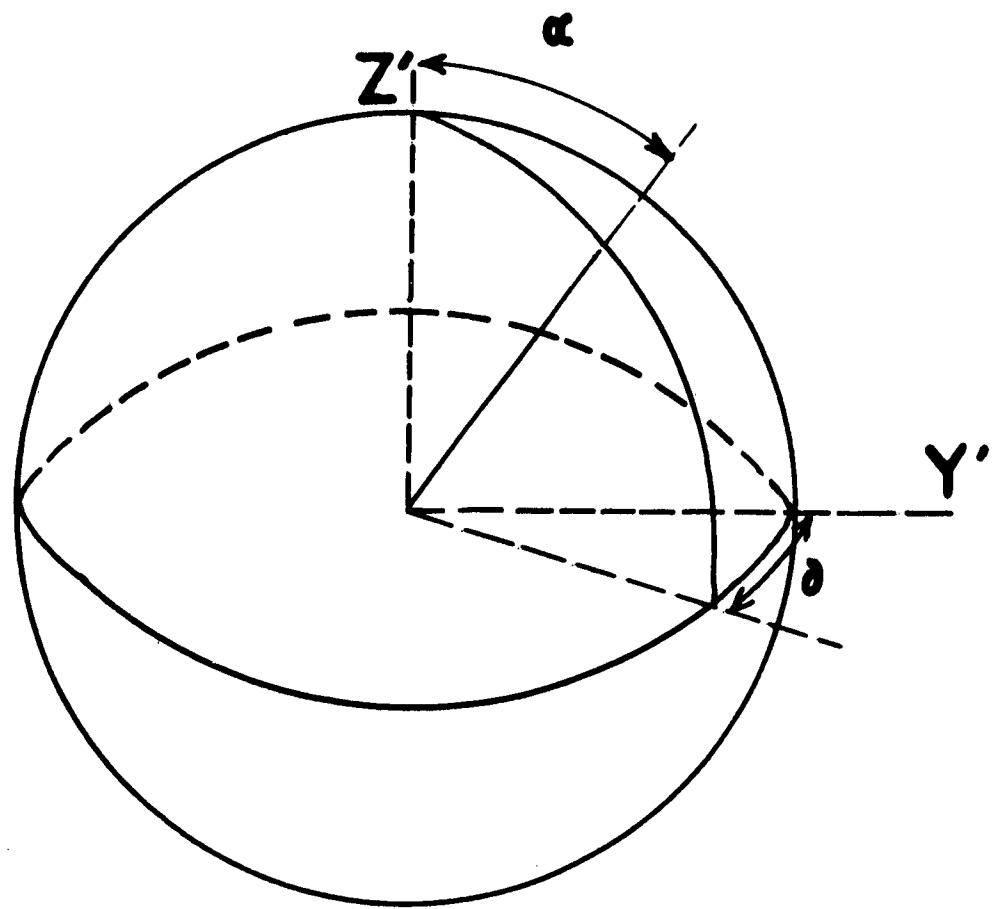


Fig. 2

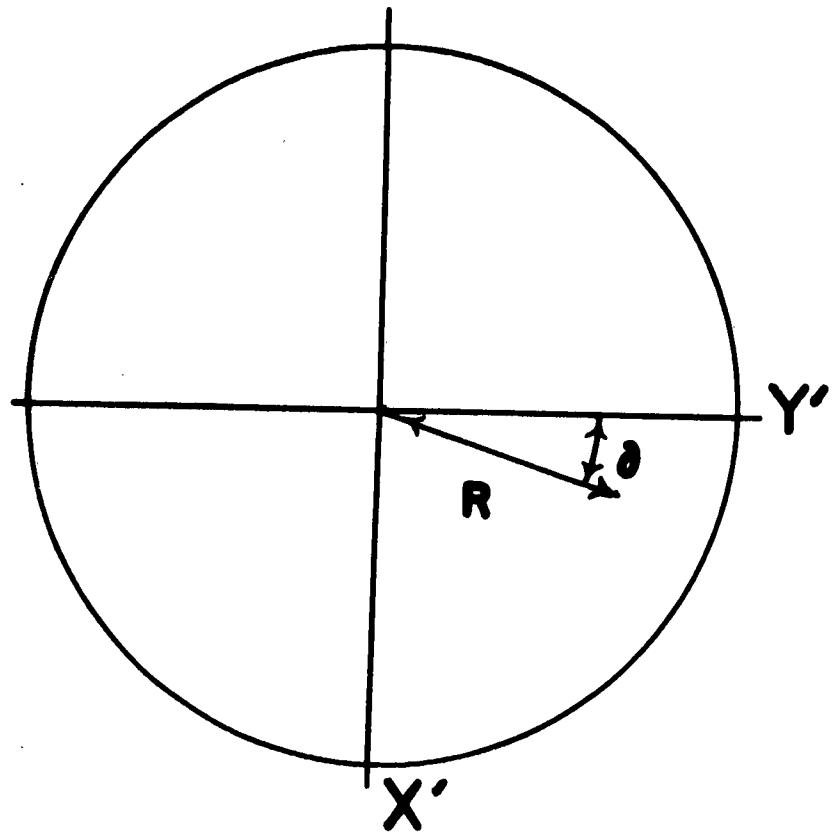


Fig. 3

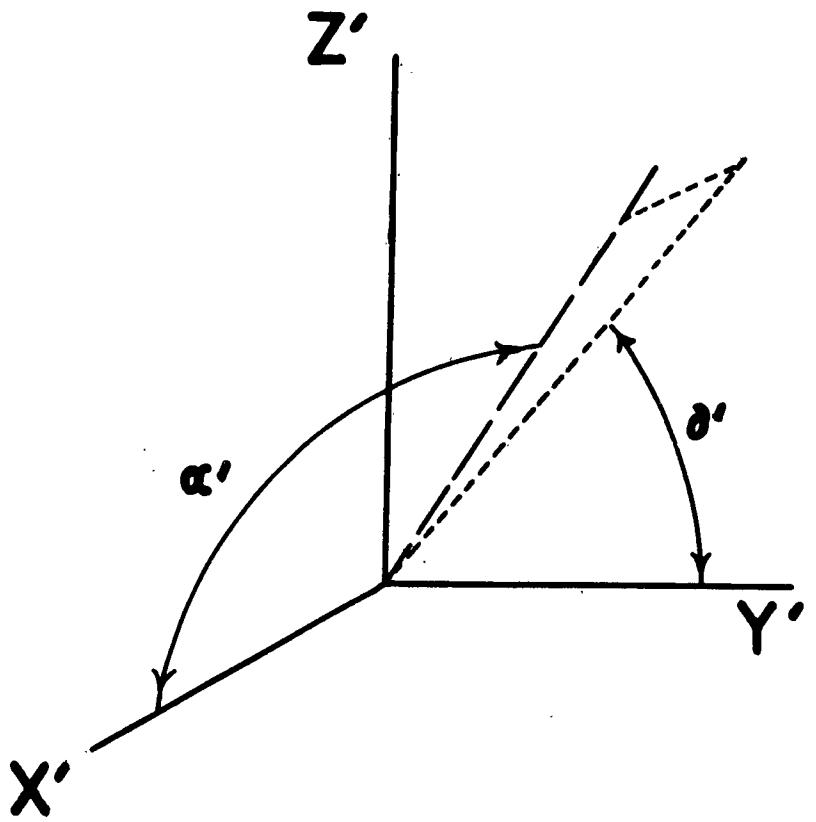


Fig. 4

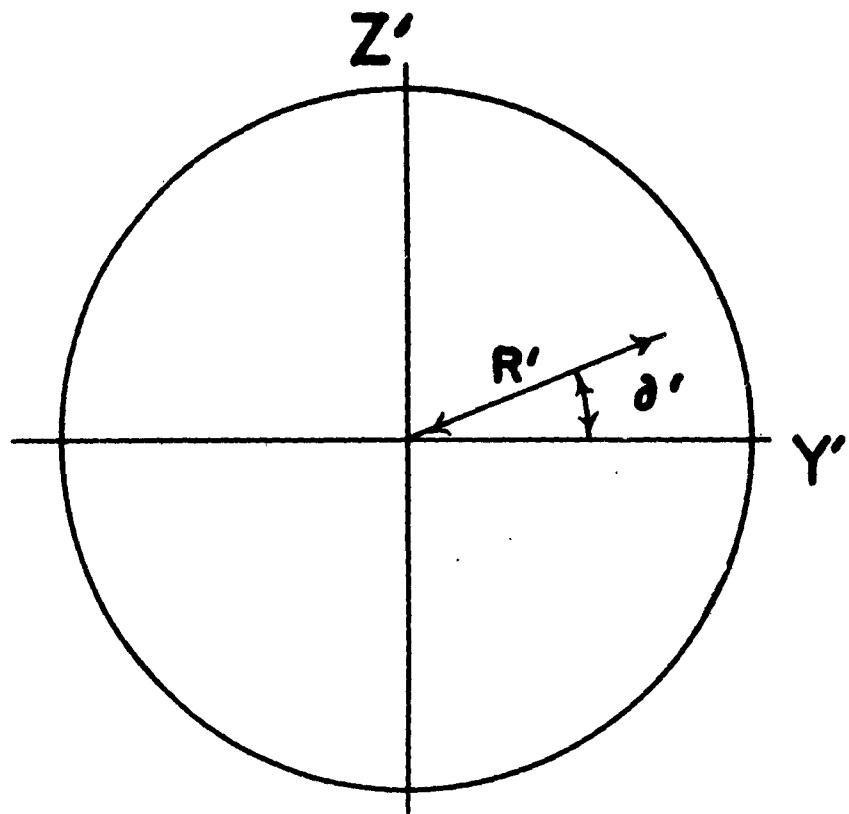
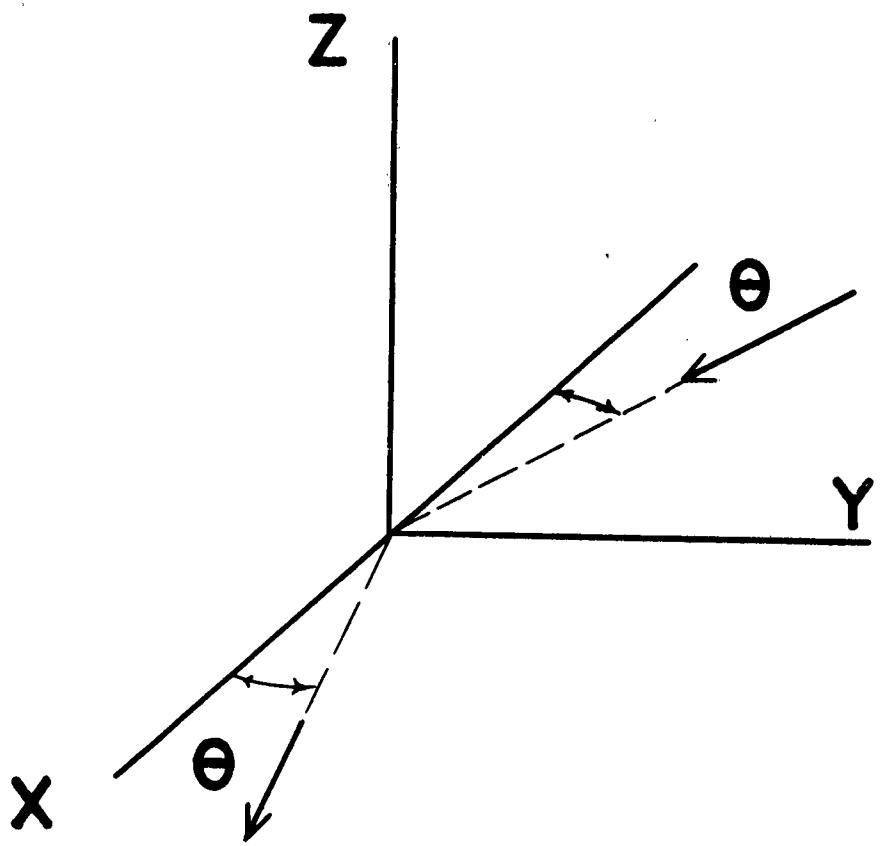


Fig. 5



**Fig. 6**

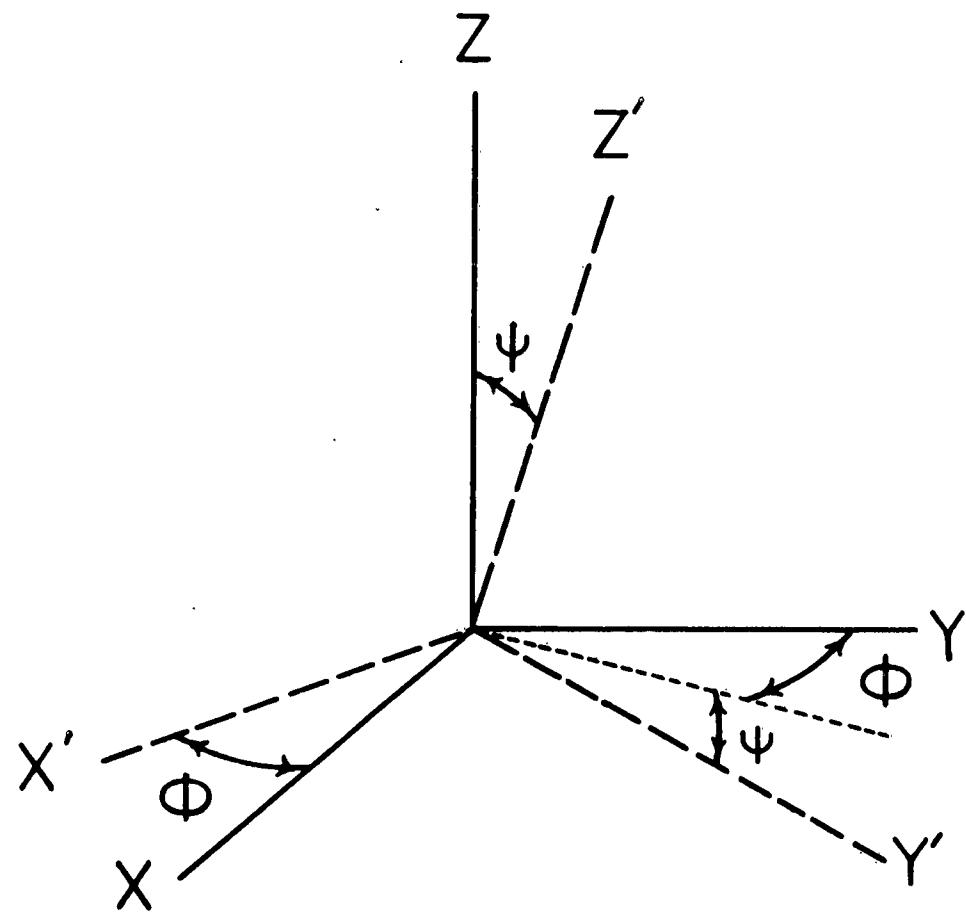


Fig. 7

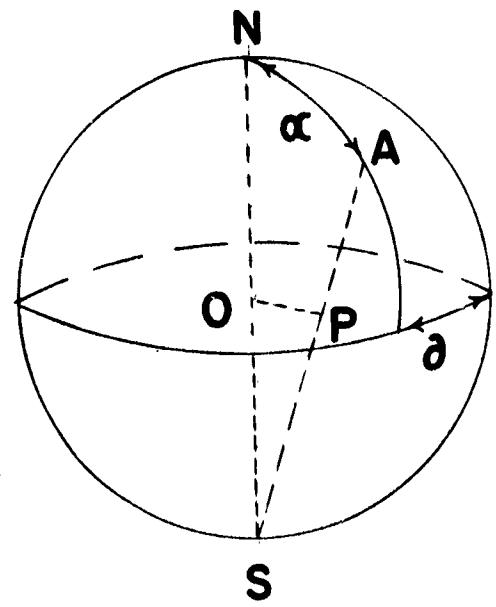
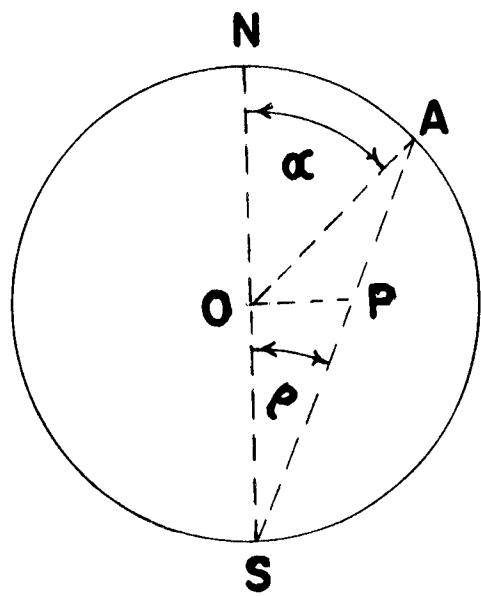


Fig. 8



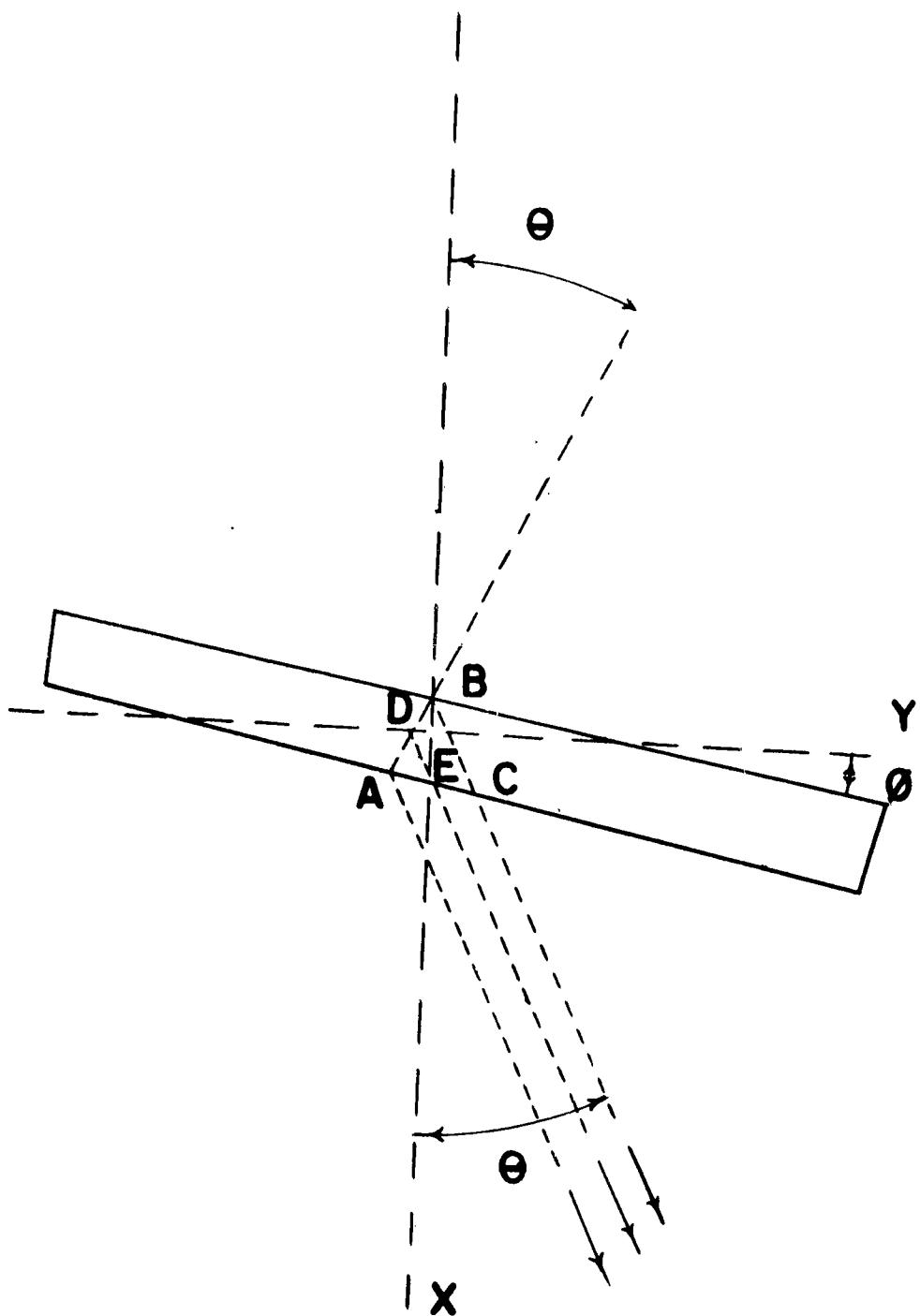
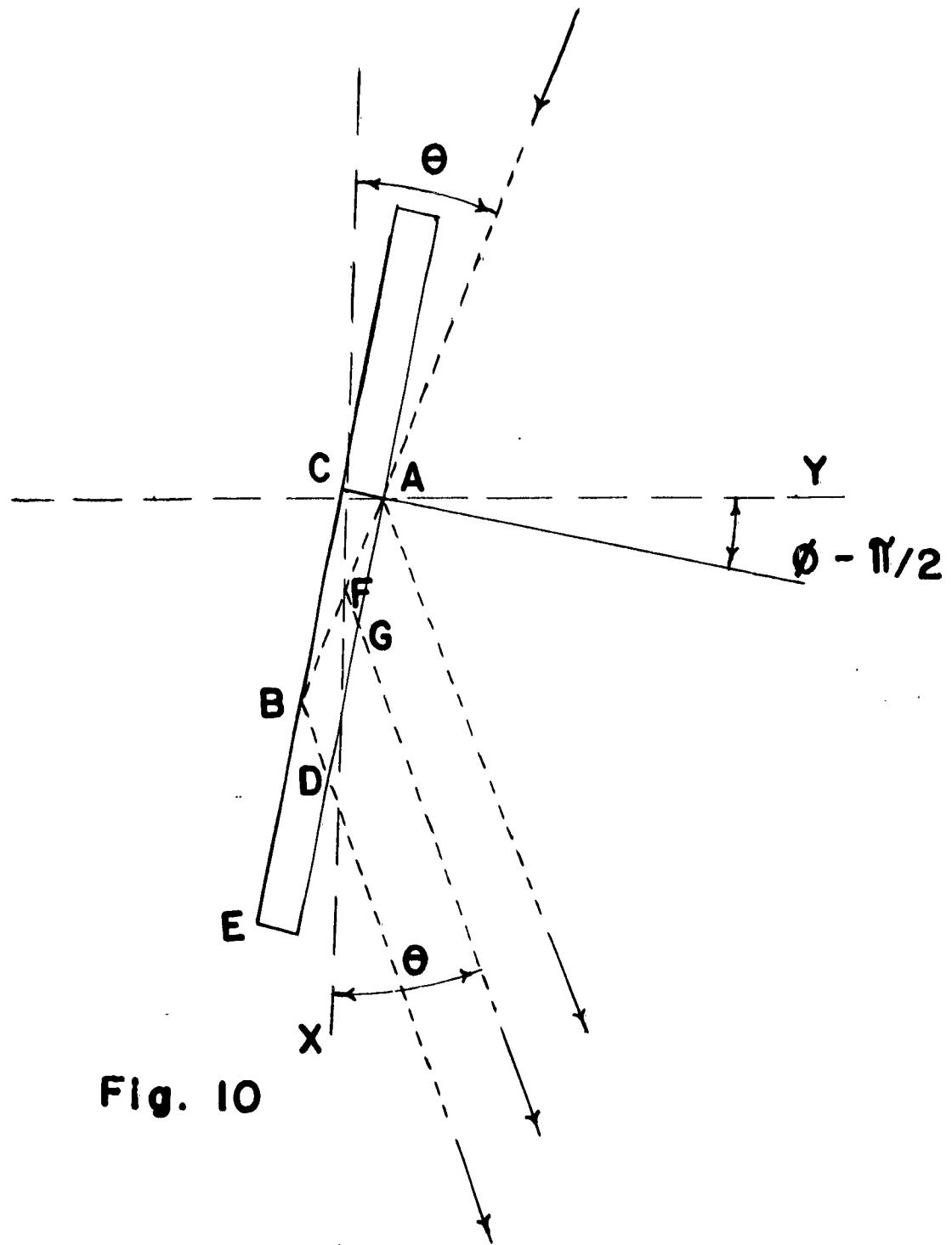


Fig. 9



**Fig. 10**

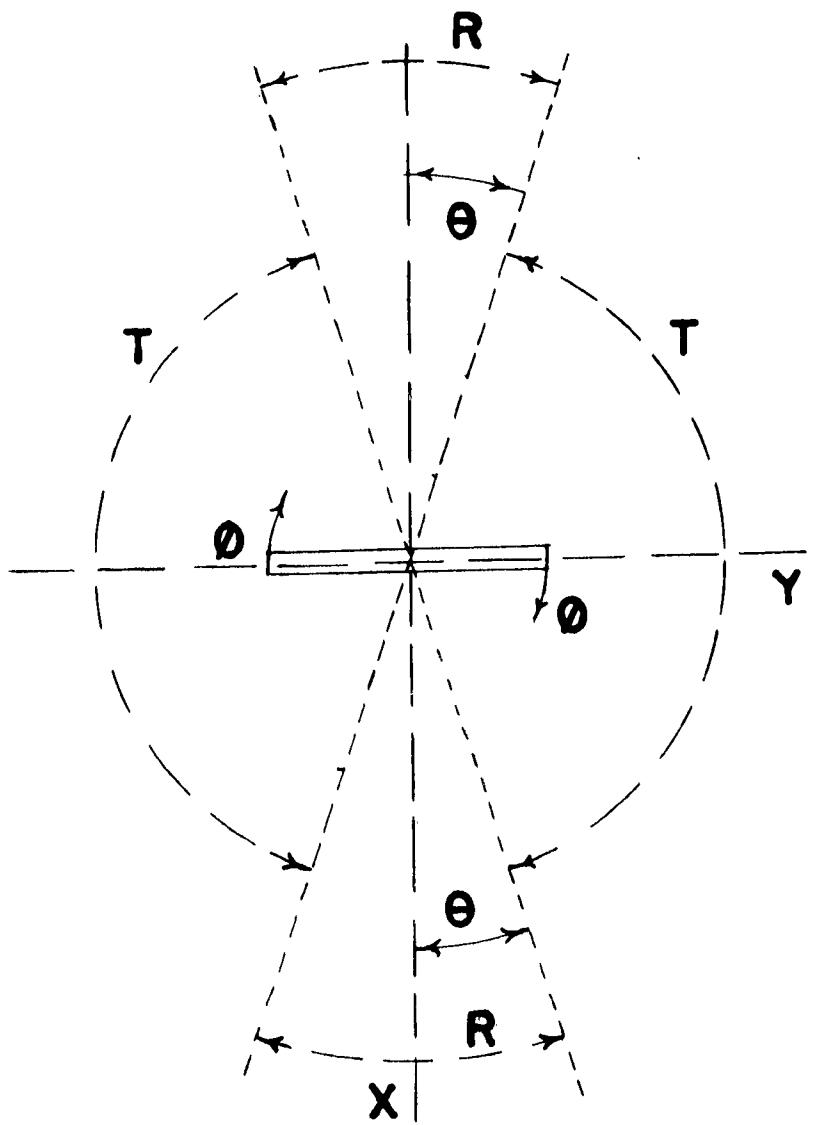


Fig. II